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               KEELE UNIV (ENGLAND) DEPT OF CHEMISTRY P BORRELL
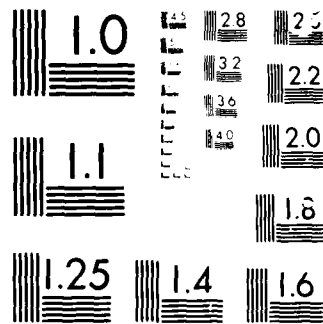UNCLASSIFIED   FEB 86 EOARD-TR-86-03 AFOSR-84-0035   F/G 7/4   NL

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University of Keele
Department of Chemistry

Kinetic and Spectroscopic Studies of Chemical Intermediates
at both High and Low Temperatures.
(A Final Report to the United States Air Force in fulfillment
of Contract AFOSR-84-0035)

by

Peter Borrell, BSc, PhD, ScD, FRSC, CChem, FRSA
Reader in Chemistry

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Contents

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1. Introduction

The aim of the funded work was to study the temperature dependence of the rate constants of a number of elementary energy transfer, chemical and chemiluminescent reactions using our combined discharge-flow/shock tube technique. The scientific purpose is to elucidate the detailed mechanism of such reactions by comparing the observed temperature dependence with current mechanistic and theoretical models since the temperature dependence, over a wide range of temperatures, can provide a crucial test of such models.

The grant was made for one year but, as it was not possible to recruit a suitable person, it was extended for a second year and used to employ a part-time postdoctoral fellow. It contributed to our group's work in a variety of ways and so this report consists of a resumé of several aspects of our work in this field during the period.

Not only has the aim of studying several high temperature reactions been achieved but we have also developed a new low temperature method for studying temperature dependences well below room temperature so that we now have the capability of measuring selected rate constants from 100 K to 1600 K.

The work has opened several new avenues for us and thus has been wholly successful.

2. Experimental Methods

(a) <u>High Temperatures</u>. The technique used was our combined discharge-flow/shock tube. The method was first devised by Hartunian, Thompson and Hewitt[1] and by Gross and Cohen[2] but has been extensively developed by us[3] in recent years. The intermediate of interest is generated in a flowing gas at low pressure by passage through a microwave discharge and the flow, containing the intermediate, is then passed along the test section of a shock tube. Pre-shock measurements of the emission as a function of length along the 5 m tube serve to establish the concentration gradient in the tube and often give better values of room temperature rate constants[4] than have been achieved previously with smaller apparatuses.

When the flow has been characterised a shock wave is propagated along the tube and the emission, or absorption, is observed as a function of time with photomultipliers placed at particular points in the tube. The records of voltage versus time from the photomultipliers are digitised and passed to a terminal for storage and subsequent

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18. Supplementary Notes

20. Abstract

The temperature dependence of the rate constants of a number of elementary energy transfer, chemical and chemiluminescent reactions was measured using a combined discharge-flow/shocktube technique. In addition, the method itself was developed to provide a low temperature (to 100 K) capability. The reactions studied were: The collisional deactivation of $O_2(b^1\Sigma_g)$ and $O_2(a^1\Delta_g)$ by N_2 and H_2; the reactions of atomic nitrogen and oxygen with air (Lewis Rayleigh and Air Afterglows); and the quenching of $O_2(a^1\Sigma_g)$ by O_2 itself. The emissivity of the 'dimol' transition of $O_2(a^1\Sigma_g)$ was also measured.

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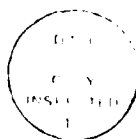
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This report has been reviewed by the EOARD Information Office and is
releasable to the National Technical Information Service (NTIS). At NTIS it
will be releasable to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication.

LARELL K. SMITH, Lt Colonel, USAF
Chief, Physics/Physical Chemistry

D. L. MOTT
Technical Information Officer

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Our contribution to the technique has been twofold: (i) to improve the signal/noise ratio by passing the flow in the opposite direction to that in which the shock wave travels; (ii) to include the pre-shock emission levels and concentration gradient in the analysis of the shock data; this is carried out by a combination of computer graphics and non-linear least squares[5] which has been found to provide reliable results from these types of experiments.

A new addition which has been aided by the grant, is the incorporation of a computer (an IBM PC-AT) to collect, store the data and also process the data locally. It is expected that the PC will also be used for apparatus control.

(b) <u>Low Temperatures</u>. For measurements below room temperature we have developed a method for cooling the low pressure flow from a discharge by using a triple-walled, double-jacketed flow tube. It is 50 cm long and fabricated from glass; the project owes much to the skill of the department glassblower, Chris Corke. The outer jacket is evacuated and coolant is passed through the inner jacket. The coolant is nitrogen which itself has been passed through liquid nitrogen. By controlling the coolant flow rate, temperatures down to 100 K can be achieved and held for long periods to ±2K.

The apparatus can also be used between 300 and 500 K by circulating silicone oil through the middle jacket. Thus our laboratory now has a capability of measuring selected rate constants between 100 and 1600 K. With the apparatus a PC has been used to collect and process data and will be used in the future for apparatus control.

For these experiments and also for some of the high temperature work a monochromator, whose purchase was aided by the grant, was used instead of filters to obtain spectral data.

3. Results

(a) The Collisional Deactivation of $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$ by H_2 and D_2.

This part of the work is one of a series of studies which we have carried out on the dectivation of the two low-lying excited states of molecular oxygen, $O_2(b^1\Sigma_g^+)$ and $O_2(a^1\Delta_g)$. The interest in these states lies in their extraordinary stability both to radiative decay and also to collisional quenching. It has been found previously that[3] for poor quenchers of $O_2(b^1\Sigma_g^+)$, such as N_2 and O_2, the rate constant rises with

temperature whereas for more efficient ones, such as CO_2 or NO, the rate constant is nearly independent or actually declines with temperature. H_2 and D_2 were chosen for study to test a recent theoretical approach with which the temperature dependence could be predicted.

Measurements of the quenching of $O_2(b^1\Sigma_g^+)$ at 293 K by H_2 and D_2 were made in pre-shock flow experiments and the results for H_2 are shown in figure 1 which gives an indication of the quality of the data. The value for the quenching constant of 2.76×10^8 $dm^3 mol^{-1} s^{-1}$ compares well with two earlier studies[6,7] and also with a very recent measurement of Sing and Sester[8].

The quenching of $O_2(b^1\Sigma_g^+)$ was then studied at high temperatures and the results for H_2 are shown in figure 2. The results provide a new case in that the rate constant increases with temperature although the molecule is an efficient quencher. Also shown on the figure are some results at low temperatures obtained by Kohse-Hoinghaus and Stuhl[9]. At 295 K these are higher than the now accepted value but the results seem to indicate a droop in the rate constant as the temperature is lowered. Clearly further experiments at lower temperatures would be worthwhile in order to establish whether the fall is real.

H_2 also quenches $O_2(a^1\Delta_g)$ and this must be taken into account in analysing the results for $O_2(b^1\Sigma_g^+)$. The reaction can also be studied directly by observing the bimolecular emission from $O_2(a^1\Delta_g)$. Figure 3 show the results for the quenching of $O_2(a^1\Delta_g)$ by H_2. The results contrast with those in figure 2 in that there is a clear Arrhenius dependence on temperature. We have found similar behaviour with other quenchers[10,11] of $O_2(a^1\Delta_g)$ and also with O_2 itself[12].

Similar results have also been obtained with D_2, which is a poorer quencher than H_2 for $O_2(b^1\Sigma_g^+)$ but is nearly the same for $O_2(a^1\Delta_g)$.

At present we are trying to apply the theory of Shin[13], modified by Maier[14], to this system to explain differences in both isotopic behaviour and temperature dependence. In the mechanism proposed the electronic energy is distributed as vibrational energy between O_2 and the quencher and the temperature dependence arises from the conversion of the energy discrepancy to translation. The initial results were encouraging[12,14] but the differences between prediction and experiment suggest that the additional temperature dependence of the electronic curve crossing should not be neglected. The H_2/D_2 results are providing an interesting test and the results will be published in full in due course.

(b)   High Temperature Studies of the Lewis-Rayleigh and Air Afterglows

The aim of our work with reactive atoms is to develop the discharge flow/shock technique for studying their reactions at high temperatures. The concentrations are monitored through their chemiluminescent emission reactions and so it is a pre-requisite to study them. Furthermore several of the luminiscent reactions have been studied extensively at room temperature[15,16] and there has been some work at high temperatures [1,2] so we have a useful comparison for our new method.

In the experiments atomic nitrogen is generated by passage through the discharge; its presence is easily detected by the well-known, yellow, Lewis-Rayleigh, afterglow which originates from the recombination of nitrogen atoms. This is then passed along the shock tube for study on its own or it is used to produce a flow of oxygen atoms. The nitrogen is titrated with nitric oxide, NO, and at the equivalence point a flow is produced of atomic oxygen in nitrogen. Addition of further NO generates the green air afterglow which results from combination of NO and O to form excited NO_2.

In initial experiments the concentration gradient along the shock tube is measured and from this the rate constants for the recombination reactions can be measured; these are found to agree well with previous determinations.

On shock heating the emission from the tube increases due to the density change and then decays away. The equation, which fits the observed emission intensity, I(t) as a function of time, t, is:

$$I(t) = R(T) \ (\rho_2/\rho_1)^2 I_{psg} \int_{t-\Delta t}^{t} (1+at)^{-1} dt/\Delta t$$

R(T) is the ratio of post to pre-shock emissivities for the afterglow; (ρ_2/ρ_1) is the ratio of post to pre-shock densities; I_{psg} is pre-shock emission intensity; Δt is the integration time of the optical system; the term inside the integral characterises the decay in time and the constant, a, is directly related to the second order rate constant for the recombination measured in the pre-shock flow. Since this is measured before every shock the comparison between the prediction from the pre-shock decay and the measured post-shock value of a provides a useful check on the validity of each record.

The values of R(T) for the green air afterglow fit the equation

$$\log R(T) = -(1.88\pm0.04) \log(T/293 \text{ K})$$

which agrees well with a similar measurement made by Hartunian, Thompson and Hewitt[1]. Their values were obtained using an optical system with different spectral characteristics and they were only able to observe the jump at the shock front so the agreement is encouraging.

However for the Lewis-Rayleigh afterglow, different results were found. Using a 579 nm filter with a bandwidth of 10 nm the emission ratio was found to be

$$\log R(T) = (-1.37\pm0.02) \log(T/293 \text{ K})$$

The ratios are appreciably lower than those of Gross and Cohen[2] who used Hartunian's apparatus. We made many experiments to check the correctness of our result. However in doing so we realised the spectrum is very structured and we devised a series of experiments to observe the behaviour of wavelengths corresponding to transitions from several vibrational levels of the $N_2(B^3\Sigma_u)$ state.

The results are shown in figure 4. It can be seen that emissivity ratio varies markedly with vibrational level, those for the highest levels falling the most as the temperature is raised.

The mechanism of the recombination of N atoms is complicated and the dispute over the electronic state formed initially, which is a precursor of the $N_2(B^3\Sigma_u)$ state, is still not resolved experimentally. It is however generally agreed that the $N_2(B^3\Sigma_u)$ state, from which the emission arises, is populated at the 6th and 12th vibrational levels, and so the other levels are populated by vibrational relaxation. The changing emissivity observed here gives an indication of the increasing rates of vibrational relaxation as the temperature is raised. The depopulation occurs faster and the emission falls. At present we are trying to fit the results with a quantitative model using the normal Franck-Condon coefficients and nearest-neighbour vibrational relaxation rates.

An unexpected result of the work concerns the fluid dynamic problem of the shock tube boundary layer in the vicinity of the contact surface. At very long times we noticed a sudden increase in the emission towards the end of a trace. We were surprised by this but, having ascertained that it occurred at times well beyond where we normally measure, we found it occurs on every shock and is quite reproducible. The peak is in the region of the arrival of the contact

surface of cold driver gas and it overlaps the arrival. It is presumably due the nitrogen atoms being forced into a boundary layer around the driver gas. That it is observed in this experiment is due to the fact that the emissivity is inversely proportional to temperature so that, as the gas is cooled, the emission rises.

This region of shock-tube behaviour has been little studied previously and our method provides a unique way of looking at the boundary layer directly. It would be very useful if the experiments could be matched with an adequate theory. At present we are simply comparing arrival times with the predictions of Mirrels[17].

(c)   The Reactions, $N+O_2$

The first test of our system on a reaction was to measure the rate constant for the reaction of atomic nitrogen with oxygen; it has been studied extensively in the past[18] and so there is a good set of data with which to compare the results.

In the experiment the flow of N in nitrogen is mixed with ~5% O_2. At room temperature in the flow tube the reaction has the following mechanism:

$$N + O_2 \rightarrow NO + O \qquad k_1$$
$$N + NO \rightarrow N_2 + O \qquad k_2$$
$$O \text{ (wall)} \rightarrow 1/2 O_2 \qquad k_3$$
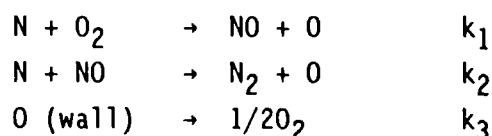
Reaction (2) is known to be very rapid so that both the decay of [N] and the formation of [O] are governed by k_1. The reaction can be followed in two ways: either by measuring the changes in the yellow emission or the change in the blue emission from the chemiluminescent N+O reaction. The two expressions for the emission are:

yellow $\quad ^{579}I(t) = k[N]^2 \quad = {}^{579}I(o)\exp(-2k_1[O_2]t)$

blue $\quad ^{403}I(t) = k'[N][O] = {}^{403}I(o) [(1+[N_0]/[O_0])\exp(-2k_1[O_2]t)$
$$- [N_0]/[O_0] \exp(-4k_1[O_2]t)]$$

The emission is measured along the length of the tube and both the simple decay of the yellow and the maximum in the blue were observed. The rate constant, k_1, was measured by fitting the data to the appropriate equations and the values from both emissions were found to agree well with each other as well as with the results from earlier work[18].

In the shock regime the wall reaction is unimportant and the

equations for the emissions become

$$\text{yellow} \quad {}^{579}I(t) = {}^{579}I_{psg}(\rho_2/\rho_1)^2 \int_{t-\Delta t}^{t} R(T)\exp(-4k_1[O_2]t)\exp(-\alpha t)dt/\Delta t$$

$$\text{blue} \quad {}^{403}I(t) = {}^{403}I_{psg}(\rho_2/\rho_1)^2 \int_{t-\Delta t}^{t} [(R(T)\ (1+[N_0]/[O_0]\exp(-2k_1[O_2]t)$$

$$- [N_0]/[O_0]\exp(-4k_1[O_2]t)\exp(-\alpha't))]dt/\Delta t$$

Again the blue emission trace can be peaked and this is observed. For each run both the blue and yellow emission records are fitted and separate estimations made of k_1 which are always found to agree.

Figure (5) shows the results together with some comparisons[18]. The agreement is good particularly when the different methods used are considered. Thus the reliability of our technique is shown and the temperature range for the reaction has been extended.

(d) **Low Temperature Studies**

These were not the major feature of the proposed work but they are related and of interest and so a brief account is given here.

To test the low-temperature apparatus measurements were made of the quenching of $O_2(a^1\Delta_g)$ by O_2 itself at temperatures between 100 and 400 K. The rate constants for quenching both by O_2 and by the wall were estimated and the quenching constant was found, to a good approximation, to display an Arrhenius dependence on temperature:

$$k/dm^3mol^{-1}s^{-1} = (1896\pm15)\ \exp[-(205\pm8)/T]$$

The measurements over this range had not been made previously but they agree well with some more recent values found by Maier[14] who studied the reaction under totally different conditions with laser excitation of O_2 at 35 atm. pressure. Our results are being interpreted using the Shin-Maier theory mentioned previously.

The apparatus was also used to measure the emissivity of the concerted 'dimol' transition of $O_2(a^1\Delta_g)$:

$$O_2(a^1\Delta_g) + O_2(a^1\Delta_g) \rightarrow O_2(X^3\Sigma_g^-) + O_2(X^3\Sigma_g^-) + h\nu$$
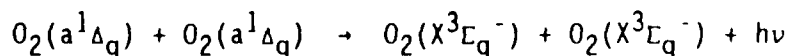
It had been reported earlier[19] that the absorptivity at 634 nm increased below 150 K. Our initial measurements using a filter with a 10 nm bandwidth showed a similar increase. However we also measured the bandwidth of the spectral peak at several temperaures and find it to depend on $T^{1/2}$. If this is taken into account then the emissivity is nearly constant with temperaure between 100 and 300 K. The results are interpreted using the collisional approach of van Kranendonk[19].

Finally meacurements have been made of the dimol emission at 579 nm from $O_2(a^1\Delta_g)(v=1)$, the vibrationally excited state. A comparison has been made with the (v=o) emission of both the emissivity and the rate constant for quenching. Under our condition the parameters for two emissions are nearly the same. This provides evidence for a mechanism in which vibrationally excited ground state molecules, $O_2(X^3\Sigma_g^-)(v-1)$, formed by quenching of $O_2(a^1\Delta_g)$ exchange vibrational energy with $O_2(a^1\Delta_g)$ to give $O_2(a^1\Delta_g)(v=1)$. The results are still being evaluated.

4.   Conclusions

The aim of the project to demonstrate the discharge flow/shock techniques as a reliable method for determining selected rate constants at high temperatures has been successfully achieved. A variety of new scientific results have been obtained and these in turn have raised questions about the theoretical models which suggest several good lines for future work.

5.   Personnel

The following were associated with various parts of the project.

Dr Peter Borrell, the Principal Investigator, was awarded an ScD degree by the University of Cambridge in 1984; The Royal Society have recently made him an award to enable him to study in Göttingen with Profesor J. Troe.

Dr Patricia Borrell, was the part-time Research Fellow employed for the work; she has worked with shock tubes and in particular the discharge flow/shock tube technique for nearly twenty years, and has many publications to her credit.

Dr Donald Richards obtained his doctorate for the high temperature work on $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$. He is now with Proessor D.

Setser in Kansas.

Mr Andrew Billington, a PhD student constructed the low temperature apparatus and obained the low-temperature results. He expects to submit his thesis in 1986 and go to the United States.

Professor Nathan Rich, from the Department of Physics, Memorial University, Newfoundland, visited our group for two months in 1985 and made substantial contributions to the dimol emission work.

6.   Conference Presentations, Publications and Forthcoming Papers.

(a)   During the course of the work papers or posters concerning the work were presented at the following:

Intenational Symposium on Gas Kinetics, Nottingham, 1984.

15th. International Symposium on Shock Tubes and Shock Waves, Berkeley, 1985.

17th. International Symposium on Free Radicals, Granby, Colo. 1985.

IUPAC Meeting, Manchester, 1985.

(b)   The following papers were published on this or related work:

67.   1984: (P.Borrell and D.T.Dixon). Electrode potential diagrams and their use in the Hill-Bendall scheme for photosynthesis. J. Chem. Educ., 61, 83-86.

68.   1984: (P.Borrell, P.M.Borrell and R.Boodaghians). A study of the temperature dependence of the quenching rate constants for singlet molecular oxygen, $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$, by NH_3. J.Chem.Soc., Faraday Trans. 2, 80, 817-822.

69.   1984: (P.Borrell, P.M.Borrell, D.S.Richards and R.Boodaghians). High temperature quenching reactions of singlet molecular oxygen. J. Photochem., 25, 399-407.

70.   1985: (P.Borrell, R.B.Boodaghians and P.M.Borrell). Temperature dependence of the collisional quenching of singlet molecular oxygen $(O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+))$ by SO_2. J.Photochem., 31, 29-36.

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(c)   The following papers are in press or preparation:

A.P.Billington, P.Borrell and N.Rich,   Low Temperature Measurements of the "Dimol" Emission of Singlet Molecular Oxygen; Proc.17th.Int.Symp. Free radicals, 1986, (in press).

P.M.Borrell and P.Borrell,   The Discharge Flow/Shock Tube as a Method for studying Contact Surface Mixing. Proc.15th.Int.Symp.Shock Tubes and Shock Waves, 1986, (in press).

A.P.Billngton and P.Borrell,   The Low Temperature Quenching of Singlet Molecular Oxygen, J.Chem.Soc.,Faraday Trans.2, 1986, (in press).

A.P.Billington, P.Borrell and N.Rich,   The Low Temperature Enhancement of the Dimol Transitions of Singlet Molecular Oxygen., J.Chem.Soc.,Faraday Trans.2, 1986, (in preparation).

P.M.Borrell, P Borrell and D.A.Ramsay, High Resolution Studies of the Near Ultraviolet Bands of Oxygen., Canad.J.Phys., 1986, (in press).

P.M.Borrell, P.Borrell, D.S.Richards and D.Quinney,   The Quenching of $O_2(b^1\Sigma_g^+)$ at High Temperatures; kinetics, sensitivity analysis and corrections., J.Chem.Soc.,Faraday Trans.2, (in preparation).

A.P.Billington, P.M.Borrell and P.Borrell,   Evidence for Vibrational Relaxation from the High Temperature Emission Studies of the Lewis-Rayleigh Afterglow., J.Chem.Soc.,Faraday Trans.2, (in preparation).

P.Borrell and D.S.Richards,   The Quenching of $O_2(a^1\Delta_g)$ and $O_2(b^1\Sigma_g^+)$ by H_2 and D_2. J.Chem.Soc.,Faraday Trans.2, (in preparation).

A.P.Billington, P.M.Borrell and P.Borrell,   High Temperature Measurements of the Rate Constant for the reaction: $N + O_2$. J.Chem.Soc.,Faraday Trans.2, (in preparation).

7. References

1. R.A.Hartunian, W.P.Thompson and E.W.Hewitt, J.Chem.Phys., 1966, 44, 1765

2. R.W.F.Gross and N.Cohen, J.Chem.Phys., 1968, 48, 2582

3. P.Borrell, P.M.Borrell, D.S.Richards and R.Boodaghians, J.Photochem., 1984, 25, 399

4. R.Boodaghians, P.M.Borrell and P.Borrell, Chem.Phys.Letters, 1983, 97, 193

5. P.Borrell, Computers and Chemistry, 1980, 4, 131

6. K.H.Becker, W Groth and U Schurath, Chem.Phys.Letters, 1971, 8, 259

7. R.J.O'Brien Jr. and G.H.Myers, J.Chem.Phys., 1972, 53, 3832

8. J.Sing and D.W.Setser, J.Chem.Phys., (in press.)

9. K.Kohse-Hoinghaus and F.Stuhl, J.Chem.Phys., 1980, 72, 3720

10. R.Boodaghians, P.M.Borrell and P.Borrell, J.Chem.Soc., Faraday Trans.2, 1984, 80, 817

11. R.B.Boodaghians, P.M.Borrell and P.Borrell, J.Photochem., 1985, 31, 29.

12. A.P.Billington and P.Borrell, J.Chem.Soc.,Faraday Trans.2, 1986, to be submitted.

13. H.K.Shin, J.Chem.Phys., 1965, 42, 59.

14. M.Chatelet, A.Tardieu, W.Spreitzer and M.Maier, J.Chem.Phys., (in press).

15. A. Fontijn, C.B.Meyer and H.I.Schiff, J.Chem.Phys., 1964, 40, 64

16. J.Anketell and R.W.Nichols, Rep.Prog.Phys., 1970, 33, 269.

17. H.Mirels, Phys.Fluids, 1966, 9, 1907.

18. D.L.Baulch, D.D.Drysdale, D.G.Horne and A.C.Lloyd, High Temperature Reaction Rate Data, 1969, 4, 11.

19. A.R.W.McKellar, N.A.Rich and H.L.Welsh, Canad.J.Phys., 1972, 50, 1

8. Captions for Figures

Figure 1.   Results for the quenching of $O_2(b^1\Sigma_g^+)$ by H_2 at 293 K.

Figure 2.   Results for the quenching of $O_2(b^1\Sigma_g^+)$ by H_2 between 500 and 1200 K. The points shown between 200 and 400 K are from reference (9) corrected to allow for their high value at 295 K.

Figure 3.   An Arrhenius plot to show the results for the quenching of $O_2(a^1\Delta_g)$ between 500 and 1200 K.

Figure 4.   The Emissivity ratios at various wavelengths, R(T), for the Lewis-Rayleigh afterglow as a function of temperature.

Figure 5.   The rate constant for the reaction of $N + O_2$ as a function of temperatures. The fall line is that given in reference (18).

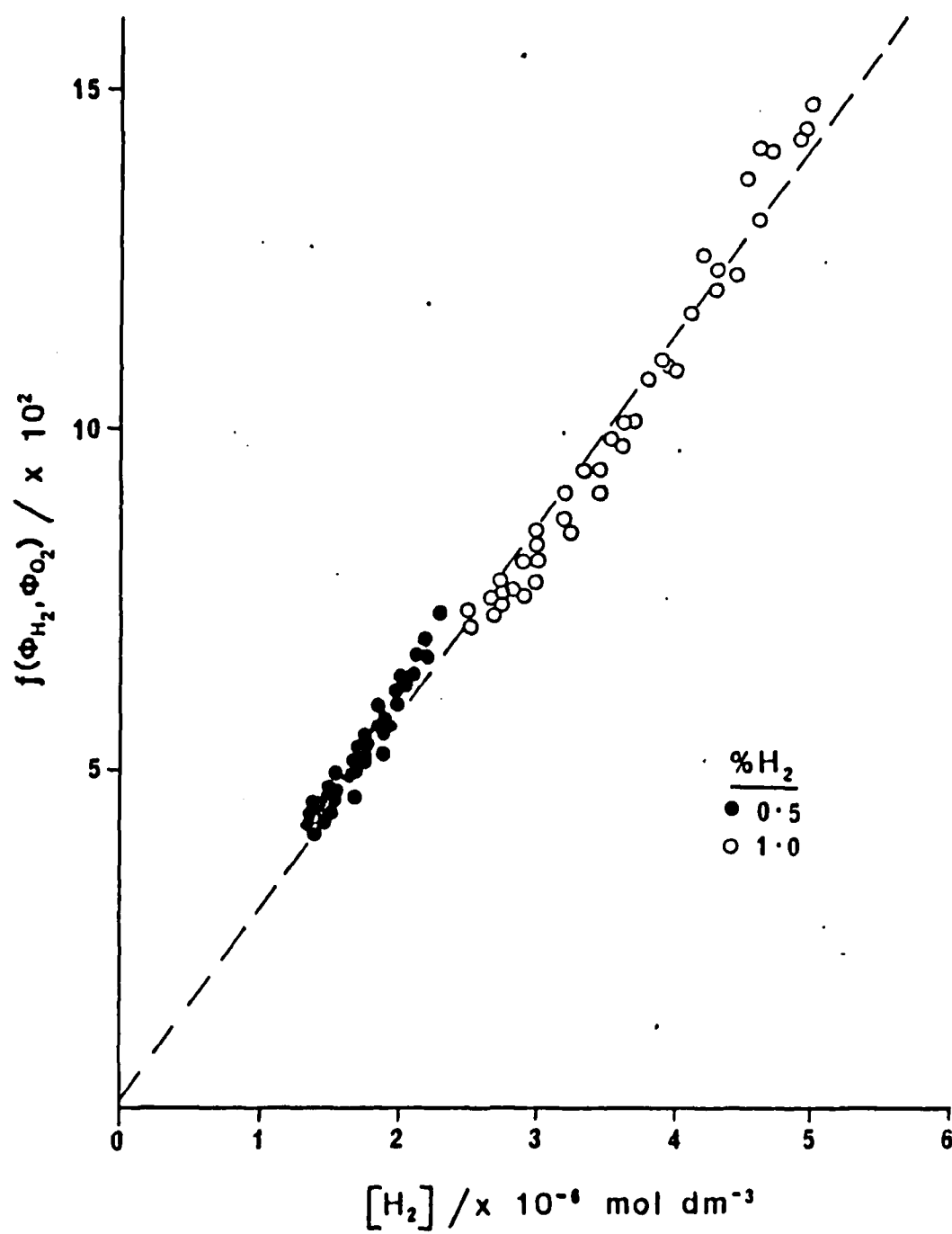Figure 1   Deactivation of $O_2(b\ ^1\Sigma_g^+)$ by H_2 at 295K

Figure 2. Deactivation of $O_2(b\ ^1\Sigma_g^+)$ by H_2
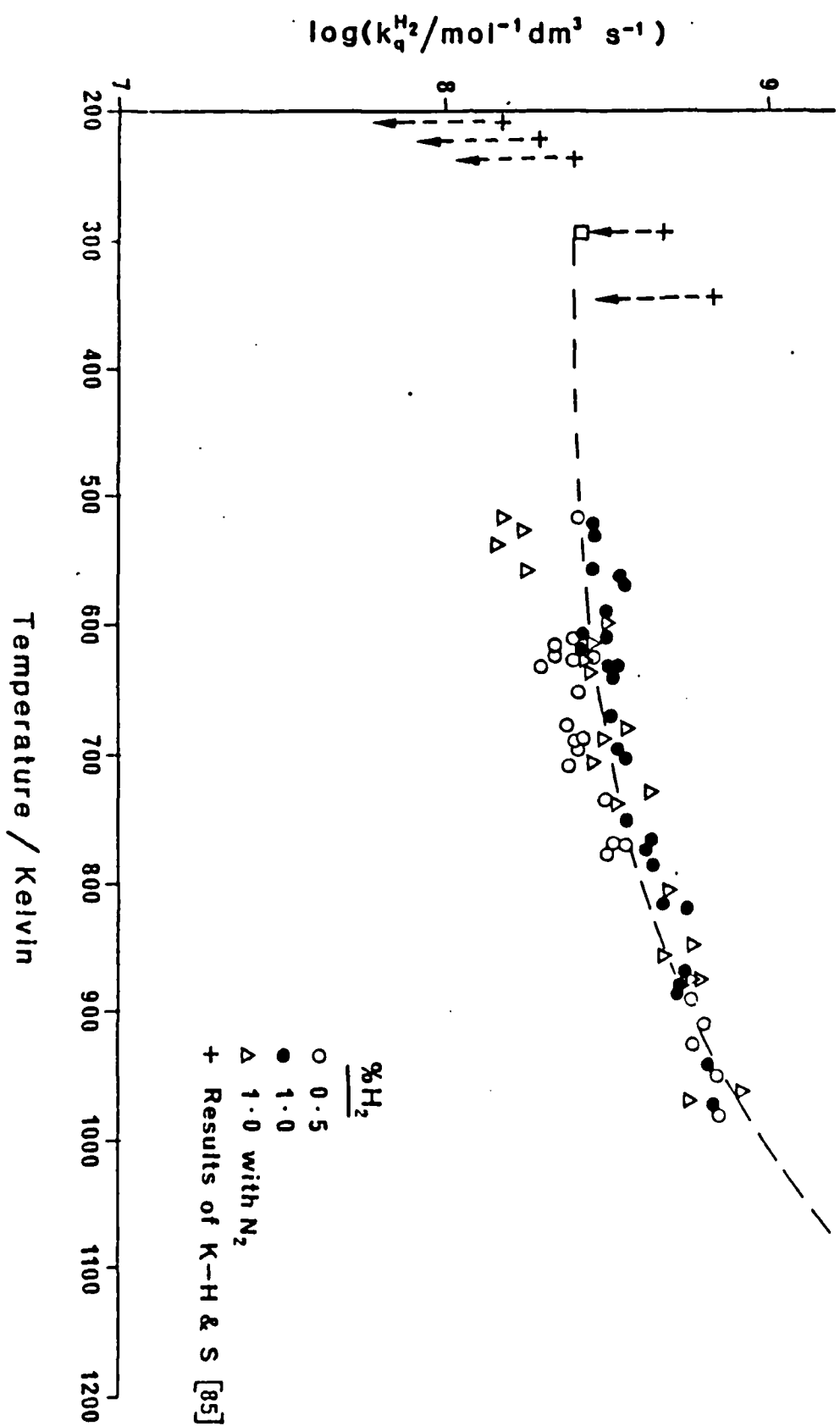
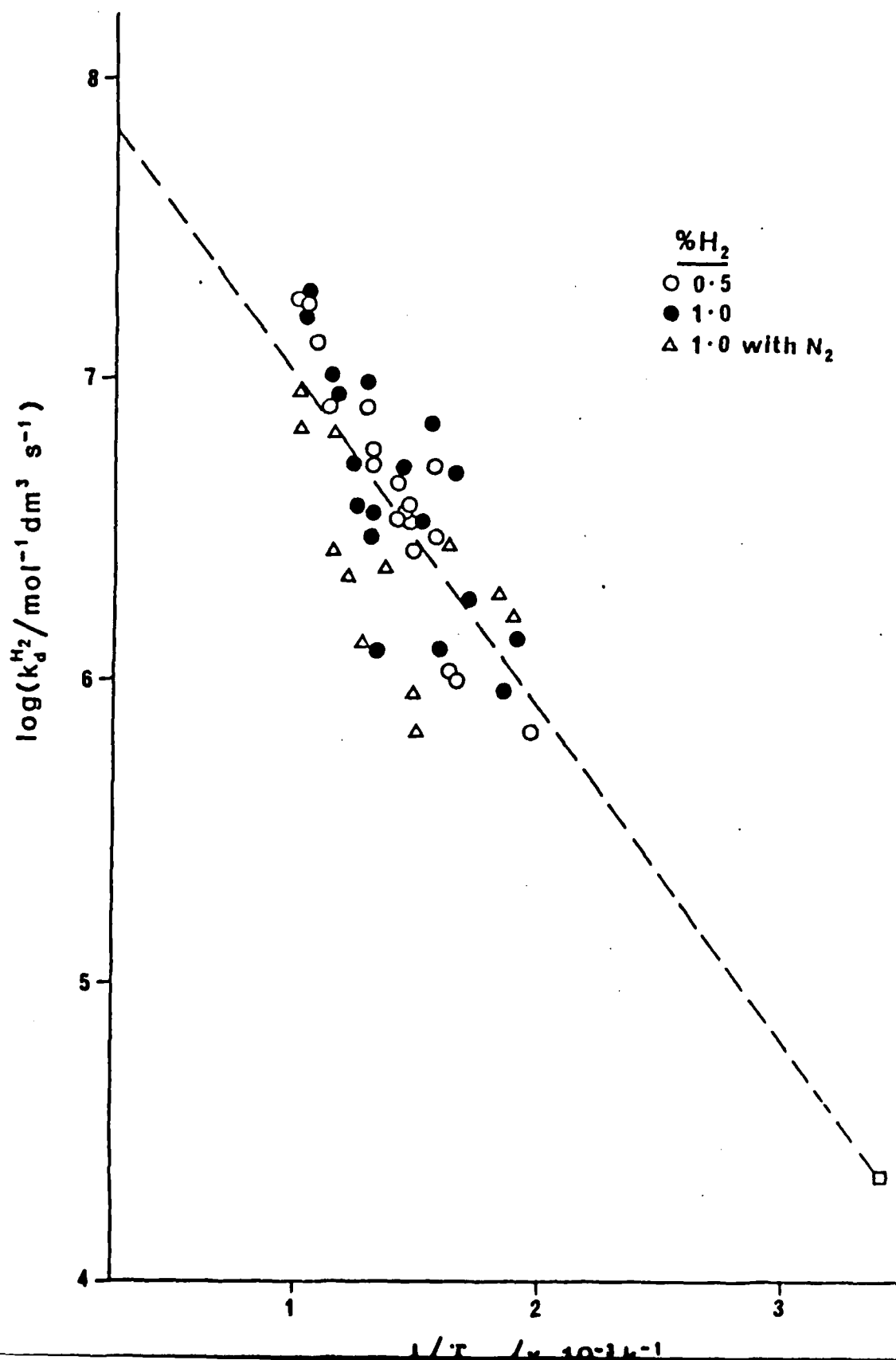Figure 3   Arrhenius plot of the rate constants for the deactivation of $O_2(a\ ^1\Delta g)$ by H_2

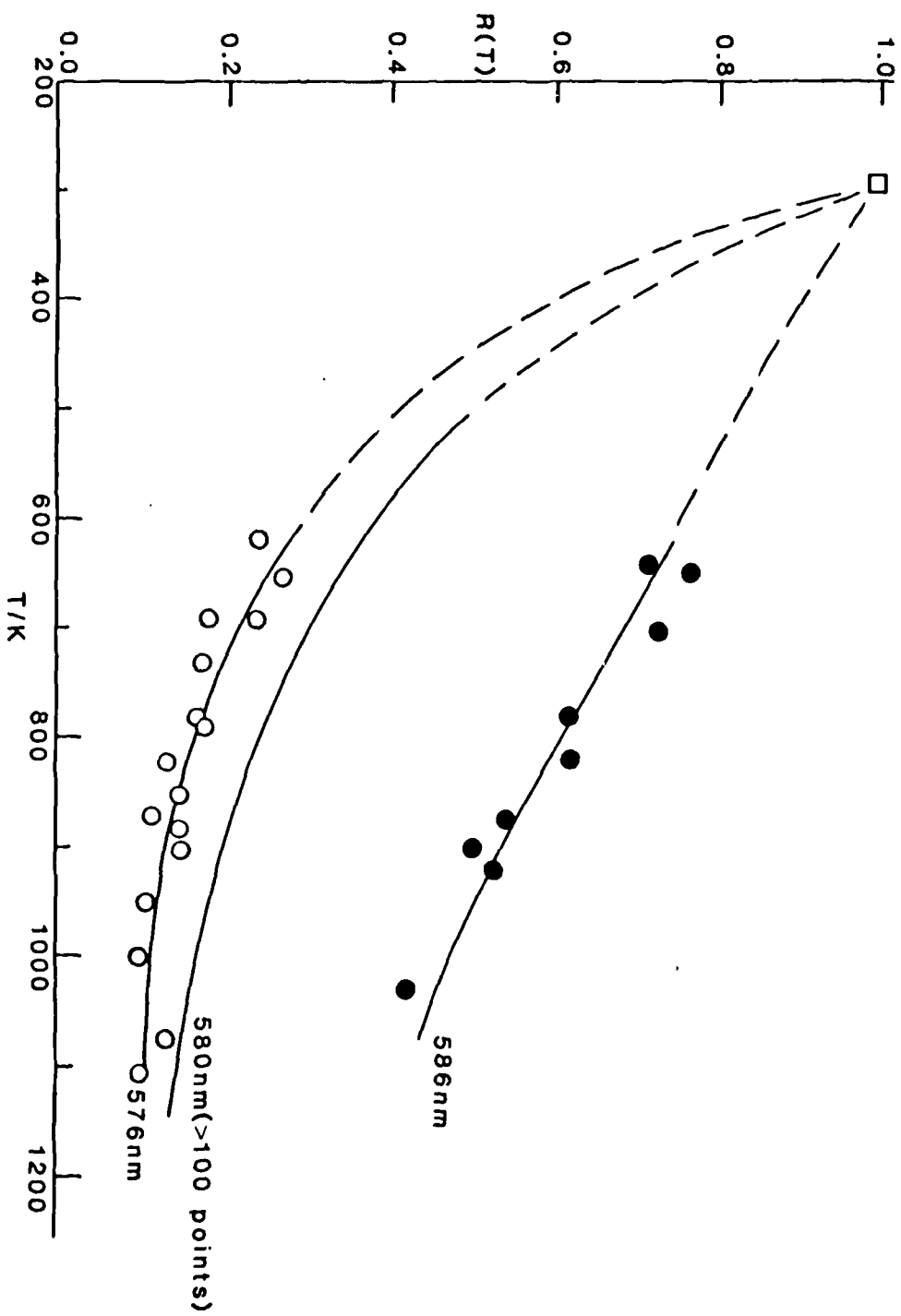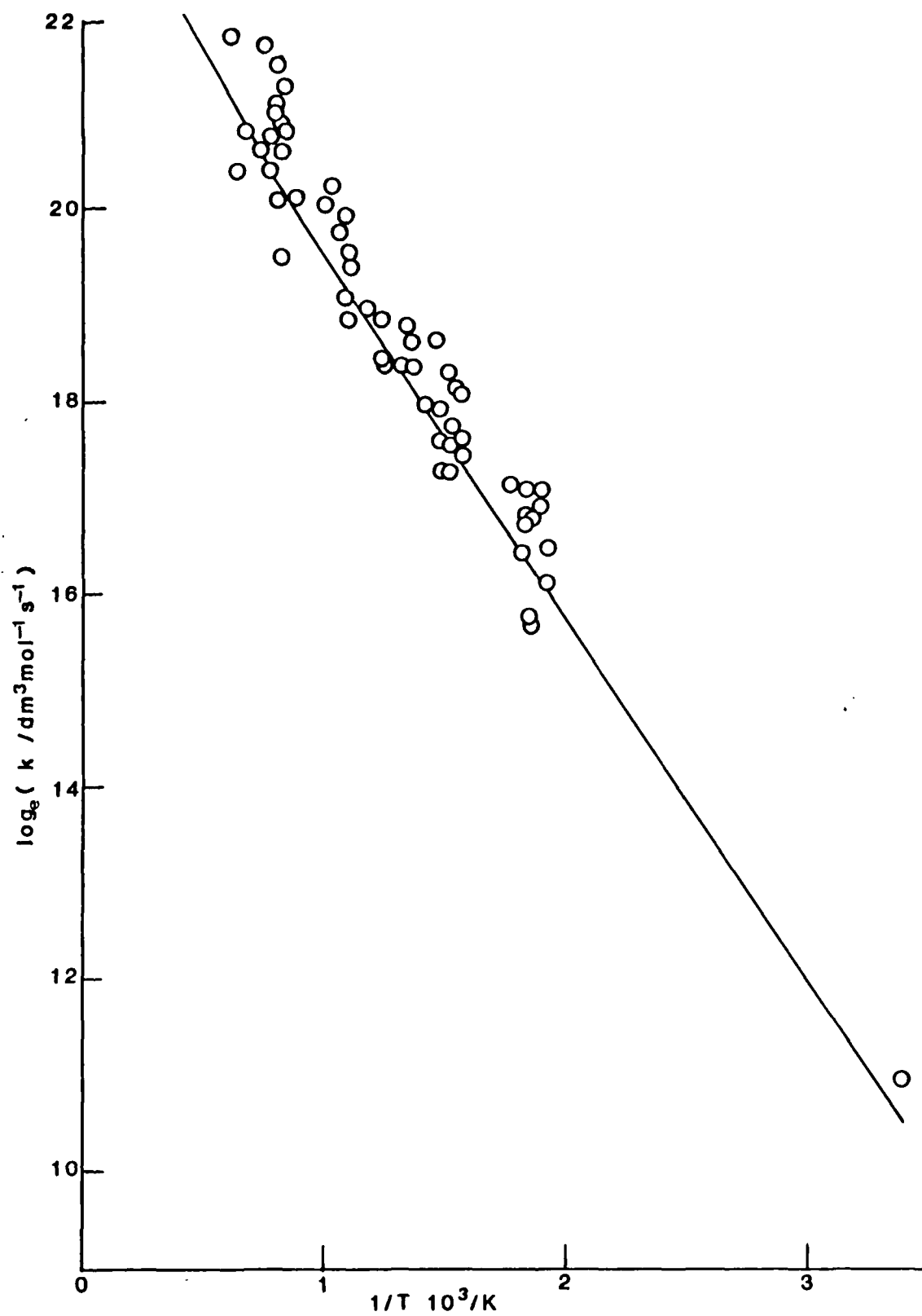Figure 4 Variation of R(T) for the Lewis-Rayleigh Afterglow.

Figure 5   Arrhenius Plot for the Reaction   N + O_2

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